

## REPORT DOCUMENTATION PAGE

Form Approved

OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 30, 1996	3. REPORT TYPE AND DATES COVERED Technical Report # 26	
4. TITLE AND SUBTITLE PHOTOGENERATED BASE IN POLYMER IMAGING AND CURING: NOVEL IMAGING MATERIAL BASED ON AN AMINE-CATALYZED ISOMERIZATION PROCESS.			5. FUNDING NUMBERS  C N00014-91-1338	
6. AUTHOR(S)  Q. Jason Niu, Edward J. Urankar, and Jean M.J. Fréchet,				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Cornell University Dept. of Chemistry, Baker Laboratory Ithaca, New York 14853-1301			8. PERFORMING ORGANIZATION REPORT NUMBER  C N00014-91-1338	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES  To appear in Polym. Mat. Sci. Eng. 1996, 75				
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale, its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  PHOTOGENERATED BASE IN POLYMER IMAGING AND CURING: NOVEL IMAGING MATERIAL BASED ON AN AMINE-CATALYZED ISOMERIZATION PROCESS.  The use of base photogenerated in situ within a polymer coating affords attractive possibilities for the imaging or curing of reactive polymeric materials. In the case of resists, photogenerated base may provide access to materials that are more resistant to airborne contaminants than the chemically amplified resists currently available commercially today. We have designed a family of novel copolymers containing benzisoxazole pendant groups that rearrange to cyanophenols in the presence of a catalytic amount of amine. The rearrangement also occurs thermally at elevated temperatures and may be easily followed by DSC. Films of the benzisoxazole-substituted copolymers containing a small amount of photogenerated base may be imaged to afford positive-tone images of the mask as the rearranged polymer is more soluble in aqueous base than the starting copolymer. At the present time the sensitivity of this resist is relatively low (ca. 100mJ/cm <sup>2</sup> ), but this may be optimized.				
14. SUBJECT TERMS Photoresist, Chemical Amplification, Photogenerated Base, solubility change, imaging, microelectronics, lithography, photosensitive coating, radiation, rearrangement			15. NUMBER OF PAGES 2	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

19960711 008

# **OFFICE OF NAVAL RESEARCH**

Grant # N00014-91-J-1338

R&T Code 313t003---07

Dr. Kenneth J. Wynne

Technical Report #26

## **Photogenerated Base in Polymer Imaging and Curing: Novel Imaging Material Based on An Amine-Catalyzed Isomerization Process**

Q. Jason Niu, Edward J. Urankar, and Jean M.J. Fréchet

Department of Chemistry Baker Laboratory Cornell University  
Ithaca, New York 14853-1301

June 30, 1996

Reproduction in whole or in part is permitted for any purpose  
of the United States Government.

This document has been approved for public release and sale,  
its distribution is unlimited.

# Photogenerated Base in Polymer Imaging and Curing: Novel Imaging Material Based on an Amine-Catalyzed Isomerization Process

Q. Jason Niu, Edward J. Urankar and Jean M. J. Fréchet

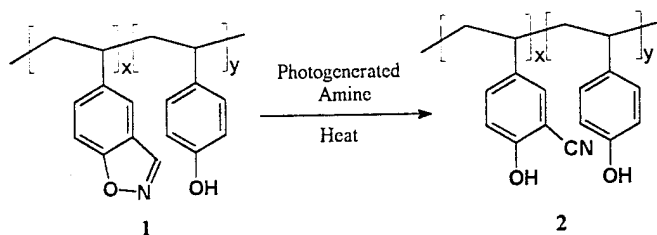
Department of Chemistry, Baker Laboratory, Cornell University,  
Ithaca, NY 14853-1301

## Introduction

Resists materials based on chemical amplification have become increasingly important in the microelectronics industry.<sup>1</sup> Generally, these materials are based on the photoinduced liberation of a strong acid which, in a subsequent catalytic process, leads to chemical changes in the resist film. Although these acid-catalyzed chemically amplified photoresists have proven to be extremely useful in manufacturing, the performance of such systems may be degraded by airborne basic contaminants,<sup>2</sup> if post-exposure processing is delayed.<sup>3</sup>

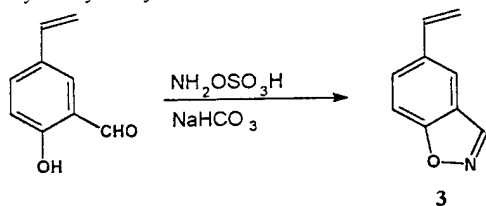
One interesting approach to avoid the problem of basic airborne contamination is to design a base-catalyzed chemically amplified process. Here a catalytic amount of photogenerated base is used instead of the acidic catalyst to achieve the chemical change in the resist materials, and we have been applying this concept several totally new imaging and resist materials.<sup>4,5</sup>

It has been shown<sup>6</sup> previously that the reaction of benzisoxazole with base is a quantitative, irreversible, highly exothermic isomerization process, proceeding by a concerted E2 mechanism to give 2-cyanophenol as the sole product. This report summarizes our recent efforts in designing a system using novel benzisoxazole containing polymers and a deep-UV sensitive amine photogenerator,<sup>7</sup> as shown below.



## Results and Discussion

**Synthesis of the Benzisoxazole Containing Polymers.** The monomer, 5-vinyl benzisoxazole, **3** was synthesized as described by Kemp<sup>6</sup> from 5-vinyl salicylaldehyde<sup>8</sup> as shown in following equation:



This compound is a colorless oil and has a very strong benzonitrile-like smell. It can be easily copolymerized with other styrene derivatives such as [(tert-butoxycarbonyl)oxy]styrene or [(trimethylsilyl)oxy]styrene **4**,<sup>9</sup> to give a high molecular weight, soluble polymer **5**, which can be hydrolyzed by dilute aqueous HCl/THF solution. The ratios of the two monomers in the feed and the copolymers, measured by both elemental analysis and DSC (Table 1), are very close, even at lower conversions suggesting that some degree of randomness prevails during monomer incorporation.

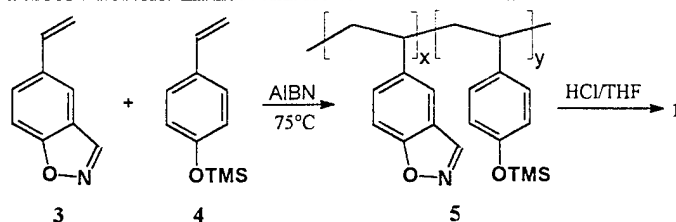


Table 1. Characteristics of the Copolymers<sup>a</sup>

$f_1^* = x$	0.33	0.50	0.67	0.33	0.50	0.67
#	5a	5b	5c	1a	1b	1c
Yield(%)	71	80	83	99	95	99
$M_w/10^3$ (g/mol)	43.7	51.2	46.7	21.4	24.9	26.9
$M_w/M_n$	1.71	1.79	2.21	1.39	1.44	1.77
$F_1^*$ (DSC)				0.32	0.48	0.65
$F_1^*$ (EA)				0.33	0.49	0.65
$T_{dec}$ (°C)				222.2	220.7	218.6

a: The polymerization was run at 75°C with 2% AIBN in 50% dioxane for 15 hours.  $f_1$  is the mole fraction of the heterocyclic monomer in the feed,  $F_1$  (DSC) is the mole fraction in the final polymer as determined by DSC (see below) or (EA) by Elemental Analysis.

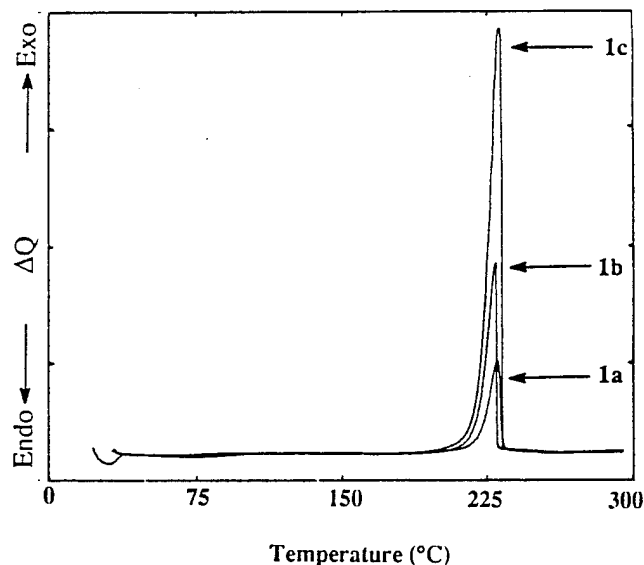


Figure 1. DSC Analysis of Copolymer 1

Polymer **1a**, **1b**, and **1c** all show excellent solubility in most organic solvents and were further evaluated as substrates for lithographic experiments. DSC traces of these polymers (Fig. 1) exhibited a large exothermic peak at around 220°C, which corresponds to the thermal isomerization reaction. This is a much higher temperatures than conventional postexposure bake temperatures (100-140°C). As expected, thermal isomerization of these copolymers **1** to **2** will not result any loss of weight, but the DSC trace clearly shows that the isomerization temperature and heat released is dependent on the content of benzisoxazole in the copolymer. The higher the ratio of benzisoxazole unit, the lower the decomposition temperature of the copolymer. Based on Kemp's calorimetric measurements of the heats of the isomerization ( $\Delta H = 26.7$  kcal/mol),<sup>6</sup> we can calculate the molar ratio of benzisoxazole in the copolymer as shown in Table 1.

**Base-Catalyzed Isomerization of Copolymer 1.** The base-catalyzed isomerization of the copolymer 1 to 2 was carried out by irradiating polymer films containing 10 wt% of amine photogenerator. As an example, polymer 1b is converted to the corresponding copolymer 2 upon exposure to 200 mJ/cm<sup>2</sup> of 254 nm irradiation followed by postexposure bake (PEB) at 140°C. Evidence for the base catalyzed isomerization is seen in the FTIR by the appearance of the absorption at 2230 cm<sup>-1</sup>, which is characteristic of the cyano functional group (Fig 2). On the other hand, the unexposed copolymer containing 10% of amine photogenerator was quite stable under thermal treatment at 140°C for 10 minutes.

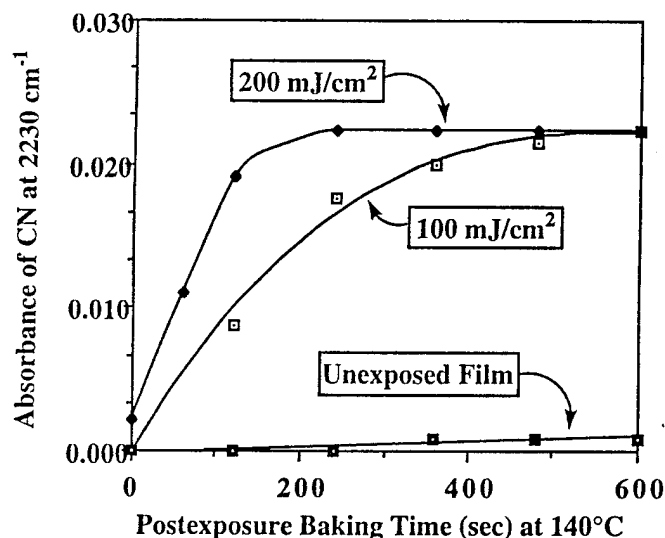


Figure 2: FTIR Study of Amine Catalyzed Isomerization of Copolymer 1b

**Lithographic Evaluation.** The photoresists were prepared by dissolving copolymer 1 in diglyme (20%) with 10 wt % photobase generator, filtering through a 0.45 micron filter, spin-coating onto silicon wafers at 2000 rpm for 30 seconds, and heating the resulting film at 100°C for 2 minutes to afford a 1.0 micron film. Postexposure baking was carried out at 140°C for 10 minutes, and 100% AZ-312 MIF solution was used as developer. The sensitivity of formulated photoresists were measured through a gradient multidensity mask (Ditric Optics) to afford a composite image with areas of different exposure doses. The less benzisoxazole content in the copolymer, the more sensitive it appear to be. For example, copolymer 1b afforded a sensitivity of 85 mJ/cm<sup>2</sup> and 1c has a sensitivity of 105 mJ/cm<sup>2</sup>. Although 33% loading of benzisoxazole copolymer 1a is most sensitive in the photoresist experiments (50 mJ/cm<sup>2</sup>), the film itself slowly dissolves in the developer because high content of phenol units. The copolymer with greater than 50% loading of benzisoxazole did not dissolve in the developer at all.

#### Experimental Procedure.

**Preparation of 5-vinyl benzisoxazole (3).** 5-Vinylsalicylaldehyde was synthesized according to the method of Wulff<sup>8</sup> in good yield. In a 500 ml Erlenmeyer flask, 6 g (0.040 mol) of the 5-vinylsalicylaldehyde was dissolved in ethanol (ca. 15 ml) such that the solution was saturated at 25°C. To this stirred solution was added 6 g (ca. 1.4 equiv.) of hydroxylammonium O-sulfonate. After several minutes, 250 ml of dichloromethane was added, the mixture was cooled in ice, and a solution of 9 g of sodium bicarbonate in 100 ml of water was added. The resulting mixture was heated to room temperature and stirred at that temperature for about 2 hours. The dichloromethane layer was then separated and dried over sodium sulfate. Purification of the crude product by column chromatography with dichloromethane as eluent gave 3.51 g (60%) of a pure product as a colorless oil. The product can also be purified by vacuum

distillation. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.67 (s, 1H), 7.65 (m, 2H), 7.54 (m, 1H), 6.77 (dd, 1H), 5.75 (d, 1H), 5.27 (d, 1H), <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 161.9, 146.2, 135.7, 133.8, 128.2, 121.7, 119.4, 114.1, 109.6. Calc. for C<sub>9</sub>H<sub>7</sub>NO: C, 74.46, H, 4.86, N, 9.65. Found: C, 74.36, H, 4.69, N, 9.72.

**General Procedure for the Synthesis of Copolymers (5) of 5-vinyl benzisoxazole and [(trimethylsilyl)oxy]styrene.** The various copolymers 5 with different ratios of 5-vinyl benzisoxazole to [(trimethylsilyl)oxy]styrene were prepared by free radical polymerization in solution. For example, [(trimethylsilyl)oxy]styrene<sup>9</sup> (1.92g, 0.01 mol) and 5-vinyl benzisoxazole (1.45g, 0.01 mol) were dissolved in 3.37 g of dioxane, and stirring was accomplished by a vigorous argon flow for 15 minutes. Then 2,2'-azobis (isobutyronitrile) (66 mg, 0.00040 mol) was added to the reaction mixture and the reactor flask was sealed off and placed in a 75°C oil bath. After 15 hours, the flask was cooled to room temperature and acetone was added. The polymer was isolated by precipitation into methanol and further purified by redissolution into THF followed by precipitation into hexanes. After drying under vacuum for 24 hours, the desired copolymer (2.68 g, 80%) was obtained as a white powder. The average molecular weight (M<sub>w</sub>) and polydispersity (M<sub>w</sub>/M<sub>n</sub>) determined by gel permeation chromatography were 51,200 and 1.79, respectively.

**General Procedure for the Deprotection of Copolymer 5.** The TMS group of the various copolymers 5 with different compositions were removed by dissolving each copolymer in a dilute HCl/THF solution. For example, copolymer 5b (2.0 g) was dissolved in THF (250 ml) containing conc. hydrochloric acid (10.0 g). The resulting mixture was stirred at room temperature for 5 hours. After evaporating most of the solvent, the crude polymer 1b was recovered by dissolved in acetone and precipitated into water. It was further purified by redissolution in THF followed by precipitation into hexanes. yield 1.50 g (95%). Anal. Calc.: C, 77.22, H, 5.79, N, 4.83, Found: C, 75.80, H, 6.12, N, 4.69. M<sub>w</sub> = 24,900, D = 1.44.

#### Acknowledgements

Financial support of this research by the Office of Naval Research is acknowledged with thanks.

#### References

- MacDonald, S. A., Willson, C. G., Fréchet, J. M. J. *Acc. Chem. Res.*, **1994**, *27*, 151-158 and references therein.
- MacDonald, S. A., Clecak, N. J., Wendt, H. R., Willson, C. G., Snyder, C. D., Knors, C. J., Deyoe, N. B., Maltabes, J. G., Morrow, J. R., McGuire, A. E., Holmes, S. J. *Proc. SPIE*, **1991**, *1466*, 2-12.
- Hinsberg, W. D., MacDonald, S. A., Clecak, N. J., Snyder, C. D. *Proc. SPIE*, **1992**, *1672*, 24-32.
- Willson, C. G., Cameron, J. F., MacDonald, S. A., Niesert, C. P., Fréchet, J. M. J., Leung, M. K., Ackman, A. *Proc. SPIE*, **1993**, *1925*, 354-365.
- Leung, M. K., Fréchet, J. M. J., Cameron, J. F., Willson, C. G. *Macromolecules*, **1995**, *28*, 4993-4700.
- Casey, M. L., Kemp, D. S., Paul, K. G., Cox, D. D. *J. Org. Chem.*, **1973**, *38*, 2294-2301.
- The amine photogenerator is N-[[[2-Nitrobenzyl]oxy]carbonyl]-2,6-dimethylpiperidine, prepared from 2-nitrobenzyl alcohol with known procedures. a. Cameron, J. F., Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4303-4313. b. Mochizuki, A., Teranishi, T., Ueda, M. *Macromolecules*, **1995**, *28*, 365-368.
- Wulff, G., Akelah, A. *Makromol. Chem.* **1979**, *179*, 2647-2651.
- a. Uhrich, K. E., Reichmanis, E., Heffner, S. A., Kometani, J. M., Nalamsasu, O. *Chem. Mater.* **1994**, *6*, 287-294. b. Jenkins, A. D., Petrak, K., Robert, F., Walton, D. R. M. *European Poly. J.* **1975**, *11*, 653-655.